PHENOLS IN TOBACCO SMOKE - POSSIBLE ROUTE FOR THEIR SYNTHESIS FROM ADDED SUGARS

M. Nikolić - Faculty of Agriculture, Nemanjina 6, 11081 Beograd
D. Djoković - IHTM, Studenski trg 16, 11000 Beograd
M. Džemidžić-Faculty of Agriculture, Zagrebačka 18, 71000 Sarajevo

SUMMARY

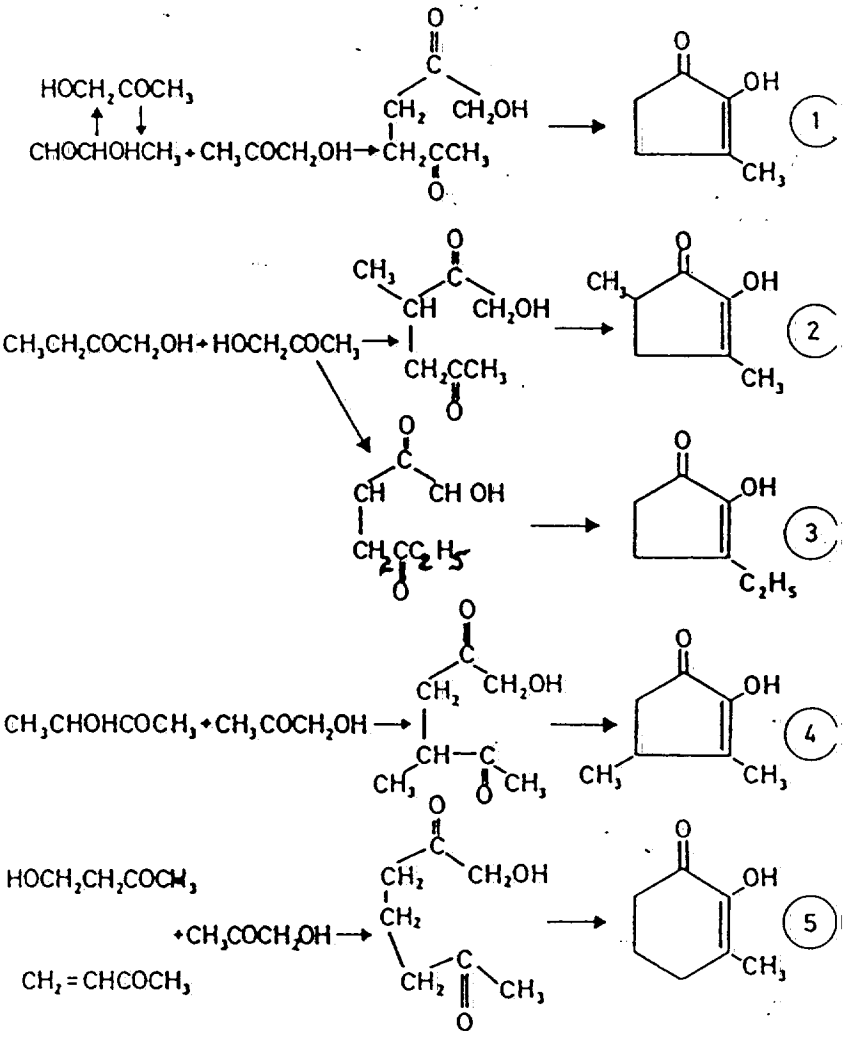
The phenol content of cigarette smoke condensate (CSC) from cigarettes made of Burley tobacco treated with four types of sugar casings has been determined by GC. As the increase was up to 10 % and the pH of the samples between 5,20 - 5,50 we supposed that base-catalyzed sugar degradation can be an explanation for phenols arising by pyrolysis. By identification of components of the weak acid (WAc) fraction of CSC (MS - identification), particulary by identification of 3-methyl 4,4-dimethyl-2-cyclohexene-1-one and 2-cyclopentene-1-one-2-hydroxy-3-methyl, and some other cyclic diketones, we consider this possibility confirmed.

INTRODUCTION

A survey of literature indicates that 5-methylfurfural and 5-hydroxymethylfurfural are the major products of sugar pyrolysis (4, 6, 13). Chemical changes under conditions of weakly acidic media are either dehydratation of monosaccharides or reactions with amino compounds (Maillard reaction - 2, 9). In more acidic or alkaline media the process of caramelization can be directed more towards aroma formation or more towards browning pigment accumulation. Increasing interest for treating lower grades of Burley tobacco, especially in Yugoslavia, with casings extended our efforts to identify some other mechanisms of sugar pyrolysis. In such cases the lower absorbing power of tobacco cell tissue retains sugars more at the leaf surface; the pH is near to neutral or slightly alkaline and additives increase a high-temperature thermolysis (5). We will report the results of our investigation of the WAc fraction of CSC of Burley tobacco treated with sugars under supposedly base-catalyzed degradation.

BASE-CATALYZED SUGAR DEGRADATION

A suitable model system for base-catalyzed fructose degradation was reported by Philip Shaw and coworkers (10). Under initial weakly alkaline conditions, with no extra addition of bases, the major porducts of degradation were as shown in Figure 1.



Under nonoxidative conditions in slightly alkaline media at elevated temperatures hydroxyaldehydes and hydroxyketones arise from cleavage of the carbon chain of sugars. Since enolization is not restricted to any part of the molecule and, since water elimination is not restricted in amount, even the spectrum of primary cleavage products is remarkable. By aldol condensation and intramolecular Cannizaro reactions (Fig. 1)

Figure 1: Base-catalyzed sugar degradation

these highly reactive products provide a great number of other products, for example cyclopentenolones (1).

EXPERIMENTAL

Cigarettes

Burley tobacco, $U_{1/3}$ grade, was sprayed with concentrated aqueous solutions of p.a. fructose (D), glucose (E), saccharose (C) and bonbon syrup (B) up to 25 % of tobacco dry mass. The sprayed tobacco was thermally treated under standard conditions and manufactured into cigarettes (85 mm). The cigarettes were conditioned and selected on the basis of average weight and pressure drop. The control cigarette (A) was sprayed with an equivalent volume of water.

Smoking of cigarettes

The cigarettes were smoked on a H. Borgwaldt smoking machine model RM 20 giving 35± 0,3 ml puff of two-second duration once a minute. Cigarettes were smoked to a butt length of 23 mm (CORESTA standard method).

Analytical Methods

The cigarette smoke condensate (CSC) was fractionated by the method of Snook (12). The WAc fractions were analysed by GC-chromatography on a Varian 3400 model instrument with:

- capillary column DB1
- Column conditions: initial temperature 250°C (isothermal for 3 min), 15°C/min to 300°C
- carrier gas - hydrogen, 3 ml/min

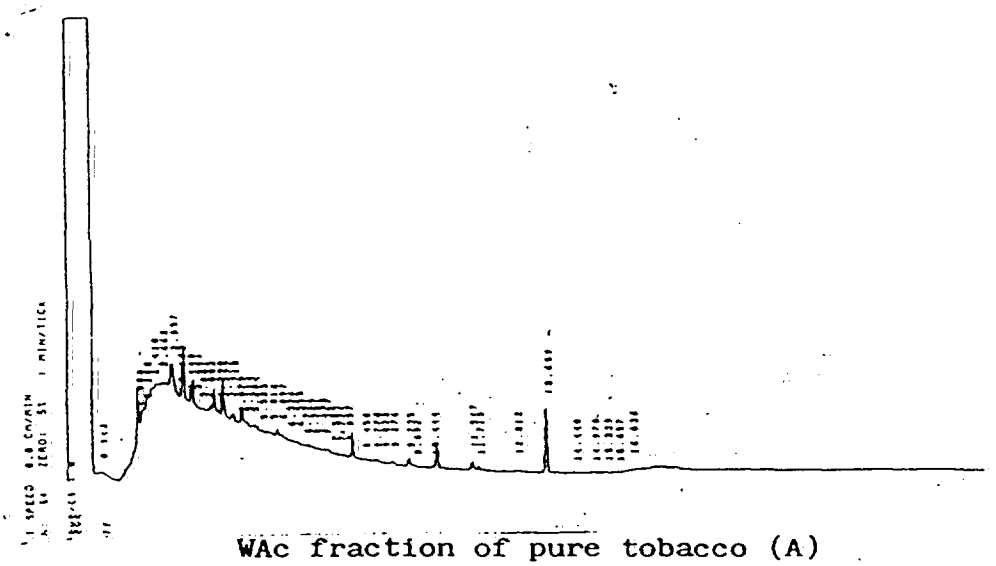
The mass spectra were obtained on a mass spectrometer Mod. Finigan MAT 8230, under the same conditions as the GC-analysis.

Thermal decomposition of tobacco was performed on Perkin-Elmer thermograph Mod. TGS-2 with air flow as in single puff.

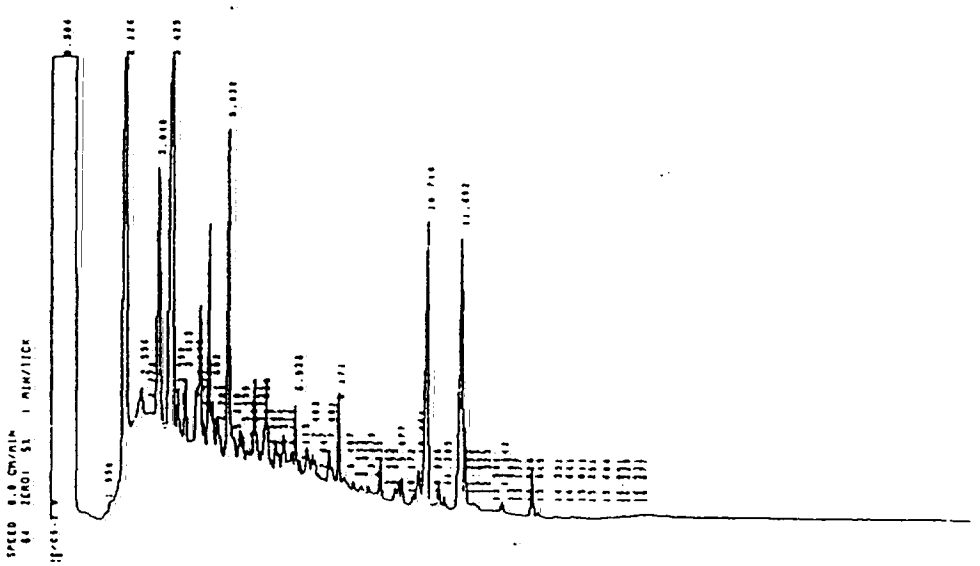
Statistical analyses of multiple correlation were done on personal computer PC-12.

RESULTS AND DISCUSSION

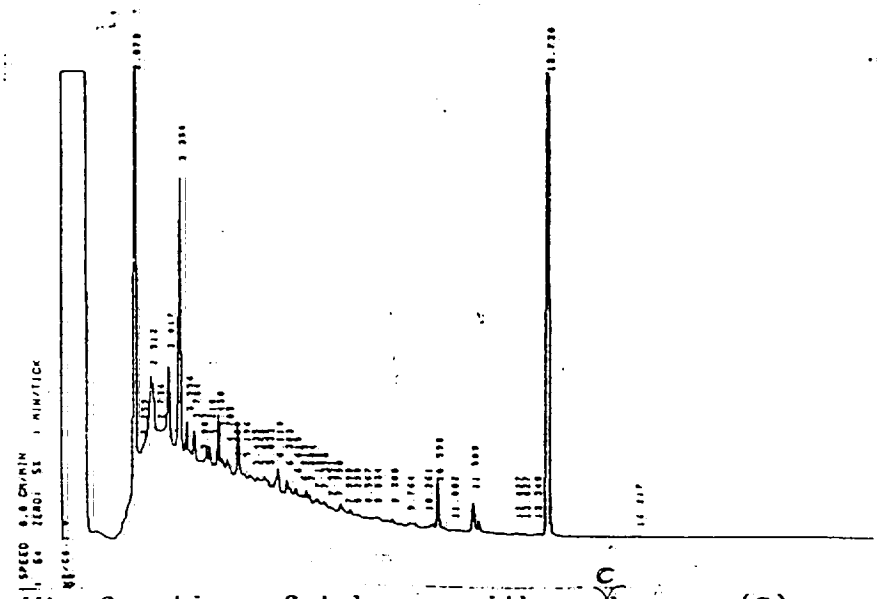
Gas chromatograms of weak acids of Burley tobacco and Burley tobaccos treated with sugars are given in Fig. 2. A-E



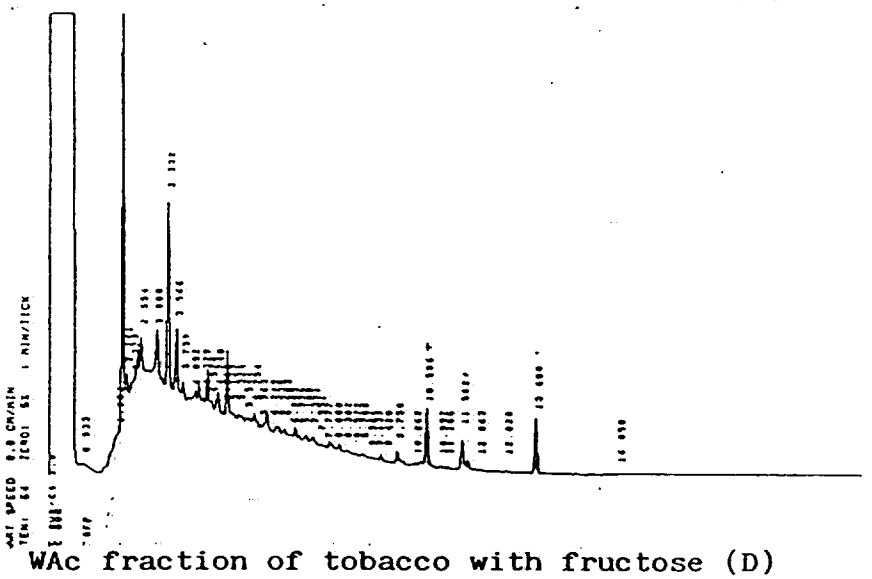
WAc fraction of pure tobacco (A)



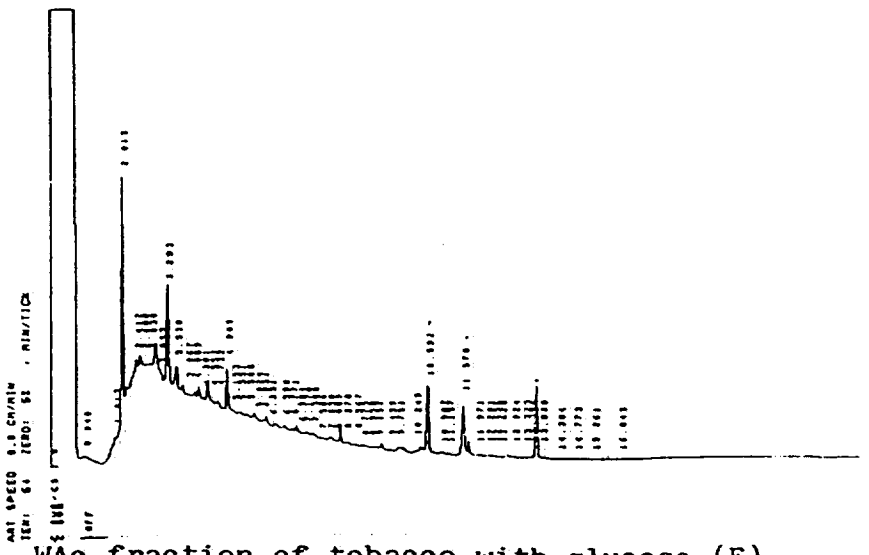
WAc fraction of tobacco with bonbon syrup (B)



WAc fraction of tobacco with sacharose (C)



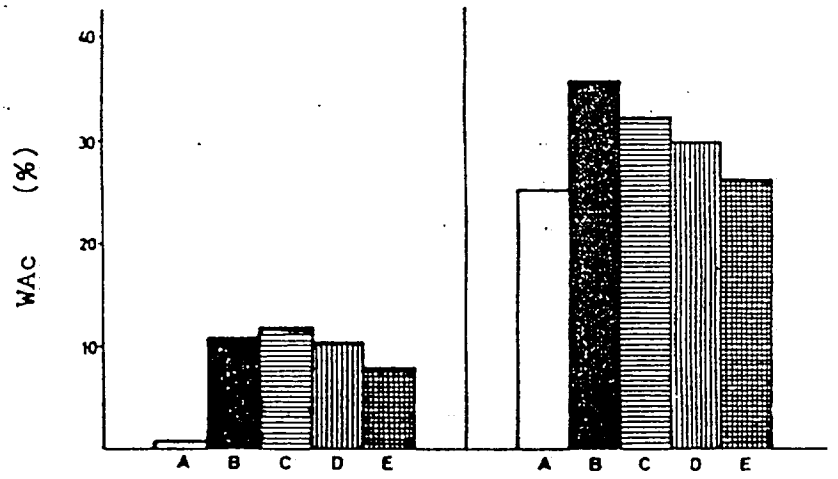
WAc fraction of tobacco with fructose (D)



WAc fraction of tobacco with glucose (E)

Fig 2: GC of WAc fractions

It is appropriate to first examine the big increase in number of the components of the WAc fraction. This fraction of untreated tobacco is both low in number and concentration of components. We found 65 compounds of which only 20 were found at an important concentration. The WAc fraction of tobacco treated with glucose, fructose, sacharose, and sugar syrup contains 98 compounds. Among these components cyclic diketones and phenols have a significant portion. From the Figure 3 it is seen that the addition of sugars causes increase of 10,95 % in cyclic diketones and increase of 10,53 % in phenoles.



Diketones		Phenoles
A-o,87	.....	25,o6
B-10,98	.....	35,59
C-11,82	.....	32,14
D-10,22	.....	29,64
E-7,93	.....	26,01

The fact that in pure tobacco only 2-cyclopentene-1-on-3,4, 5-trimethyl was identified in low concentration of 0,87 % (MS - Fig. 4) and that in all treated tobaccos samples the 2-cyclo pentene-1-one-2 hydroxy-3 methyl (MS - Fig. 5) was identified (x) [both in concentrations up to 7,02 %], points out the presence of the mentioned mechanism in Fig. 1.

(x) in addition to above mentioned

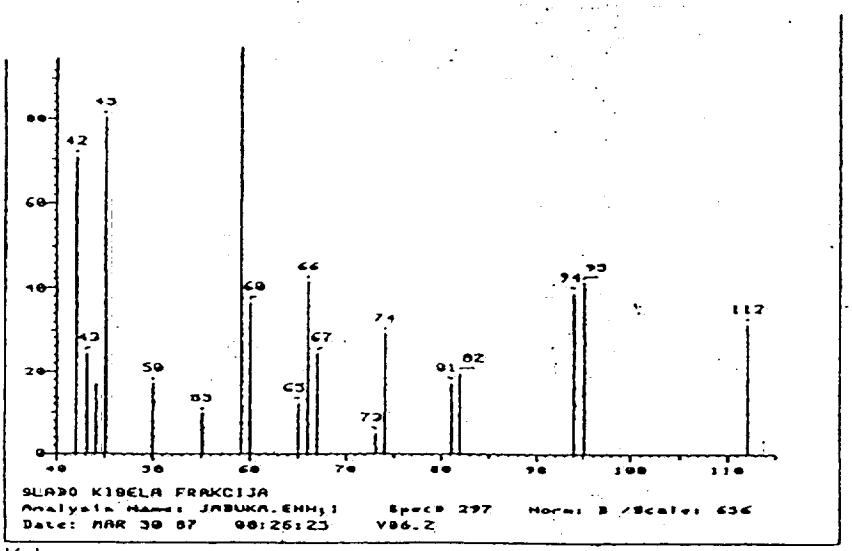


Fig. 4

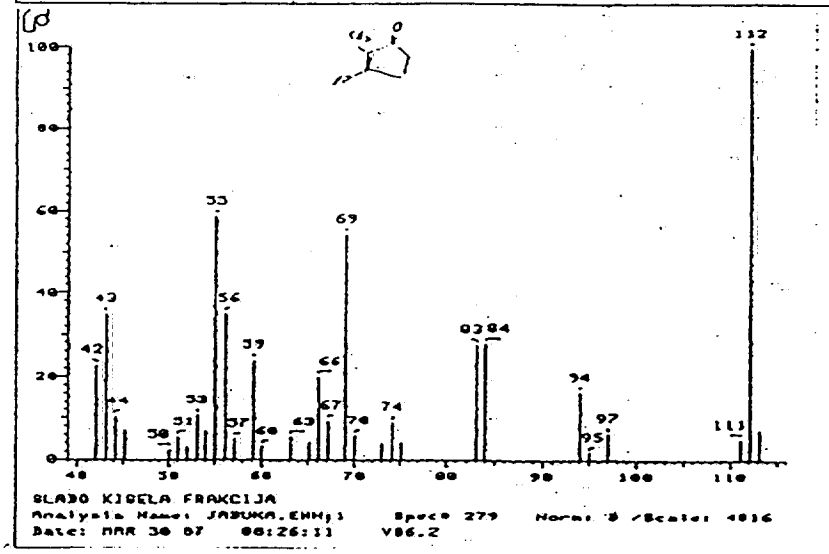


Fig. 5

The formation of a hexagon ring and further transformation into phenoles is proven, not only by increase in phenol of 10 %, but also by identification of 3-methyl-4,4-dimethyl-2-cyclohexene-1-one (Fig. 6).

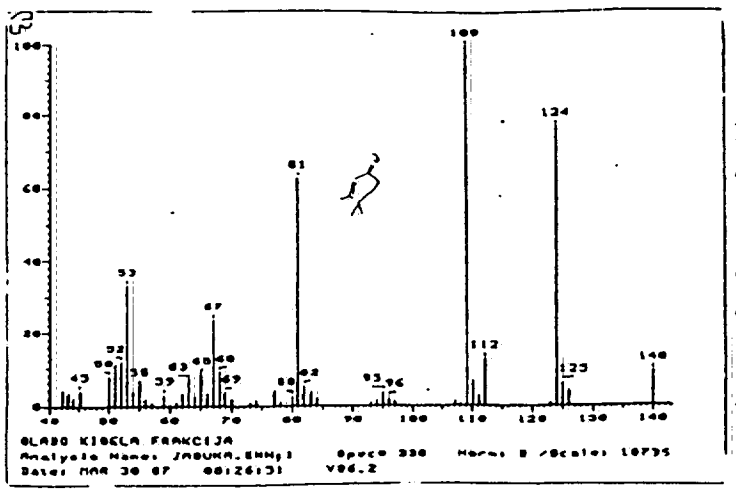


Fig. 6

These compound is, by structure, the same as compound 5 in Fig. 1. The compound was not identified in pure tobacco.

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Added sugars altered the combustion characteristics of cigarette (Table 1); they burn faster and have their maximum of weight loss in the temperature zone 350-500°C which is by some authors characteristic for phenol synthesis.

Table 1 :

Weight loss as determined by TGA.

a - temperatures of weight losses
b - % of weight loss

Ubrzek / Temp.	A		B		C		D		E	
	a	b	a	b	a	b	a	b	a	b
100			60 90	2 9	81,5	4				
200	150	9	110 120 137	11 15 23 2	138	8	110 200	49% 58%	119	23,6
300	258	16,4	201 250	38,5 46,2	287	22,8	280	72,2	212 299	52 68,3
400	322 378 390	27,5 42,5 45,1	370	61,3	318	31,1			357	74,5
500	440	51					420	87,4	426,8	78
600			550	92,5	506	60,08	524	98,2	536	96
650	630	80%			639,8	80				

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